

Development of ceramic floor tile compositions based on quartzite and granite sludges

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Abstract

In the present work, industrial sludges derived from cutting and polishing natural stones (granite and quartzite) were characterised in terms of particles size distribution, chemical and mineralogical composition, and thermal behaviour and their potential to be incorporated as main components in red-clay-based stoneware tiles was evaluated. High levels (60–70 wt.%) of incorporation were attempted aiming at designing new formulations intended to be less expensive and possess better final properties (lower water absorption and higher flexural strength) in comparison to an industrial reference body used in the production of rustic tiles by extrusion, characterised 8–9% water absorption and a flexural strength of 17–18 MPa. Extruded rods of different formulations were produced and fired at 1100 °C, 1125 °C, 1150 °C and 1200 °C. The experimental results showed that all the new formulations performed better with the most significant improvements being obtained with incorporation of granite sludge. Flexural strength values more than triplicate and water absorption decreased by more than one order of magnitude in comparison to the reference paste. The new products fulfil the requirements of the ISO 13006 standard, group BIa (porcelain tiles).

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1. Introduction

The natural rock extraction and transformation industry represents an important field in world's economy. Rock production increased from 1.80×10^6 tonnes/year in the 1920s decade to 81.25×10^6 tonnes/year in 2004 and it is expected to reach 450×10^6 tonnes/year in 2025. During the same period of about 80 years, the world's production of granite increased from 0.175×10^6 tonnes/year to 33×10^6 tonnes/year.¹ According to 2005 statistics,¹ Portugal is one the world's biggest natural rock producers (10th position, 2.45×10^6 tonnes, 2004) and exporters (8th position, 1.15×10^6 tonnes, 2004), positioned in the 3rd position among European countries.

According to INETI report,² the transformation of the extracted ornamental rock origins residues produced during sawing, cutting and polishing processes. In the case of granite transformation industry, it is estimated about 25% of rejected material during sawing process and about 15 wt.% during

cutting and polishing and about 1% during finishing process. According to this report, the transformation process of granite produces about 0.1 m^3 of mud for each ton of processed rock. The transformation industry of industrial rocks, as quartzite, involving less processing steps, produces about 1% residues.²

Land filling is the actual main destination for rock residues. The disposal of inert sludges puts serious environmental and health concerns, creating necrotic conditions for flora and fauna while, after drying, fine particles can be deposited in the lungs of mammals via breath. On the other hand, considering that some natural raw materials used in traditional ceramic industry derive from the decomposition of the rocks, a somewhat similar mineralogical composition between both should be expected. This means that these inexpensive residues can be regarded as good substitutes for the costly raw materials, therefore preserving the mineral resources, solving environmental problems, while lowering the production costs.³

Prior literature reports show that this approach has been already attempted with different degrees of success in the production of several kinds of building ceramic products. In 1999, Vieira et al.⁴ used recovery wastes from primary rock industry

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to produce tiles and flooring by pressing and sintering in the interval 1150–1170 °C obtaining water absorption values lower than 0.5%. Two years later, Hernández-Crespo et al.⁵ used ash of municipal solid wastes and two different granite sawing residues to fabricate porcelainized stoneware showing properties similar to conventional material. Granite and marble industry rejects were used by Mothé et al.⁶ and Acchar et al.⁷ to produce ceramic material. Monteiro and co-workers⁸ evaluated the effect of granite powder waste incorporation in a red ceramic body: ceramic formulations comprising from 0 to 40 wt.% granite waste were prepared and sintered in an industrial furnace at 970 °C. The results showed that granite incorporation in red clay formulations can improve extrusion process, facilitate drying stage and decrease water absorption of final product. In 2005, Menezes et al.⁹ studied the incorporation of granite sawing wastes up to 35% in ceramic bricks and tiles compositions. The results showed that ceramic compositions with additions of granite wastes could be used to produce wall and floor tiles, which after firing at 1200 °C exhibited water absorption values lower than 3%.

This work is focused on the valorisation of wastes derived from cut and polishing of ornamental rocks of granite and quartzite through its incorporation as alternative raw materials in stoneware formulations for floor and wall tiles production. The final properties were evaluated through several types of characterization tests in order to choose the best formulations. The main goal was to achieve a formulation with a residues content as high as possible without sacrificing the final properties of the products, preferentially with some improvements of its physical or aesthetical properties^{10–12} in comparison to a reference commercial paste used by Ceralfa (Oliveira do Bairro, Portugal) in the production of rustic ceramic tiles by extrusion. The reference paste, intended to be replaced by a new suitable formulation, exhibited high water absorption values (8–9%) and poor bending strength (17–18 MPa).

2. Materials and experimental procedure

The starting raw materials for the new formulations were a red clay (RC) supplied by Argilacento (Pombal, Portugal), a granite sludge (GS) from Incoveca (Viseu, Portugal), and a quartzite sludge (Qz) supplied by Piçarra & Ribeiro (Aveiro, Portugal). For comparison purposes, a red paste (CF) being already used by Ceralfa (Oliveira do Bairro, Portugal) for the production of rustic floor and wall tiles was also used. The details of the CF composition were not disclosed, but it included fine red clay rich in smectites, which make the past sensitive to drying, coarse low grade clay, and a fraction of milled tiles that were rejected after firing.

The granite sludge was received as filter-pressing wet cakes containing about 25% humidity and residues of metallic shot used in the cutting operation, as well as residual abrasives from polishing. In order to remove the coarser grains of metallic shot, the wet sludge was dispersed in water and passed through a sieve of 500 µm. The resultant suspension was kept under agitation while most of the remaining iron particles were removed by magnetic bars. The most part of the water of the suspension

was decanted and the remaining part was vaporized in a ventilated oven at 110 °C. Finally, the dried sludge was disaggregated in a hammers-mill and passed through a 500 µm sieve.

The sludge Qz was received as fine and “clean” material with about 20% humidity and then dried in a ventilated oven at 110 °C, milled in a hammers-mill and finally passed through a 500 µm sieve. The clay RC was dried at 70 °C to avoid the rupture of smectites’ structure. After manual removing the organic impurities of larger dimensions, it was milled and sieved as described above for the sludges.

The densities of the dried powders were determined by the water picnometer method. Particle size distribution of the raw materials was measured using a light scattering instrument (Coulter LS 230, UK, Fraunhofer optical model). Chemical composition of the sludge’s was determined through X-Ray Fluorescence Analysis (X-Ray Spectrometer, PW1400, Philips, Nederland). The mineralogical characterization and the identification of the crystalline phases was performed through a X-Ray Diffractometer (XRD, Rigaku GeigerflexD/Mac, C Series, Cu Ka radiation, Japan) and complemented with Differential (DTA) and Gravimetric (TG) Thermal Analyses (Labsys Setaram TG-DTA/DSC, France, heating rate 5°/min, 1 atm flowing N₂).

The tested compositions are presented in Table 1. Batches of ~6 kg were mixed with water (~16–19 wt.%) and homogenized using a mixer. The extruded cylinders (Ø ~10 mm, length 120 mm) were obtained according to industrial standards (laboratory extruder NR Burton on Trent, Rawdon Ltd., Moira, UK), dried (room temperature – 24 h, 110 °C – 24 h), and fired at 1100 °C, 1125 °C, 1150 °C and 1200 °C.

The bulk density of the fired samples was determined through the Archimedes’ method with Hg-immersion. Shimadzu machine (Trapezium 2, Japan, 0.5 mm/min displacement) was used to perform three-point bending strength evaluation. The presenting results are the average of more than 10 tested cylinders.

Water absorption was measured according to the ISO-standard 10545-3, i.e. weight gain of dried pellets after immersion into boiling water for 2 h, cooling for 3 h and sweeping of their surface with a wet towel.¹³

Finally, the surface fracture of samples was observed by Scanning Electron Microscopy (SEM, Hitachi S-4100, 25 kV acceleration voltage, Tokyo, Japan).

Table 1
Tested compositions (in wt.%)

Compositions	RC	Qz	GS
CF		Reference paste	
RC	100	–	–
1	30	70	–
2	35	65	–
3	40	60	–
4	30	–	70
5	35	–	65
6	40	–	60
7	30	35	35

3. Results and discussion

3.1. Characterization of raw materials

The starting raw materials presented the following values of density: 2.67 g/cm³ for the RC, which is typical for red clays (2.60–2.70 g/cm³) and 2.77 g/cm³ and 2.70 g/cm³, for granite and quartz sludges, respectively.

Fig. 1(a) and (b) shows, respectively, the differential and cumulative particle size distributions of RC, GS and Qz, after having passed through a 500 μm sieve. It can be observed that 100% of the sieved materials have maximum particle sizes below 100 μm. RC clay exhibits particle size values lower than 40 μm, which is accompanied by a bimodal Gaussian distribution centred in 11 and 25 μm. GS presents a wider particle size distribution range, with an average particle size of 18 μm while Qz shows a bimodal Gaussian distribution centred in 15 μm and in 70 μm. The percentage of clay minerals (particles with sizes <2 μm), is about 21 vol.% for RC, 23 vol.% for Qz and 17 vol.% for GS. The silt fractions (particles with sizes between 2 and 60 μm, are about 79 vol.% for RC, 80 vol.% for Qz and 78 vol.% for GS. The sand fraction (particles larger than 60 μm) is only presented in GS, in a relatively small amount of about 4 vol.%. As a reference, it is known that the rustic ceramic stoneware formulations usually contain particles with maximum size of around 500 μm. Therefore, from the granulometry point of view, it becomes obvious that these residues can be directly incorporated in stoneware tile formulations, avoiding any kind of further milling process. This enables to lower the energy costs associated with milling, permitting simultaneously to reduce the processing time as well as to save time dispended with equipment maintenance.

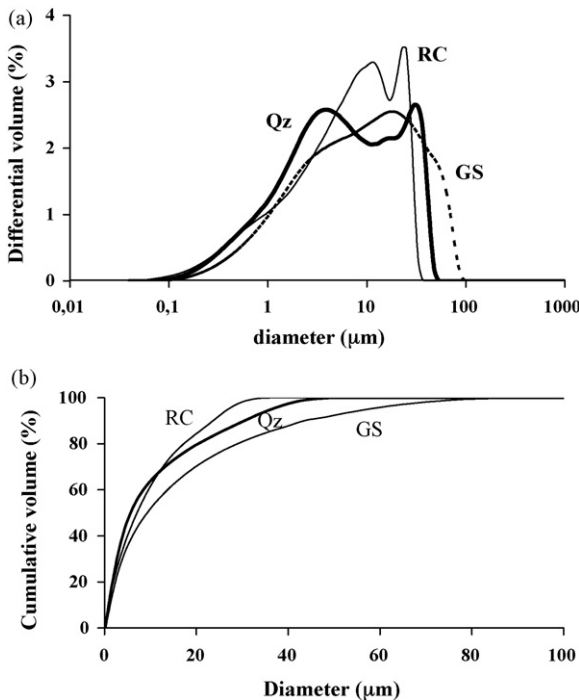


Fig. 1. Particle-size distribution of the raw materials.

Table 2
Mineral phases

Compositions	Mineral phases
RC	Quartz, kaolinite, muscovite
GS	Quartz, kaolinite, illite, muscovite, microcline, albite, calcite
Qz	Quartz, muscovite, clinochlore, microcline

Table 2 shows the mineral phases present in raw materials that have been identified by XRD. RC consists mostly of kaolinite [Al₂Si₂O₅(OH)₄], quartz [SiO₂] and muscovite [KAlSi₃O₁₀(OH)₂]; Qz is composed of quartz, muscovite, and also of clinochlore [(Mg,Fe)₆(Si,Al)₄O₁₀(OH)₈] and microcline [KAlSi₃O₈], which is feldspar materials. Feldspar minerals are typical fluxing agents, lowering the temperature required to form a vitreous phase that promotes densification. In the GS the following crystalline phases could be identified: quartz, kaolinite, illite, muscovite, feldspatic minerals such as microcline and albite [Na(AlSi₃O₈)] and, some traces of calcite [CaCO₃], probably derived from the polishing equipment or from any marble rock contamination in the cutting industrial unit. All the minerals detected in GS and Qz sludge's are usually present in the raw materials employed for the manufacture of the traditional ceramics, making feasible the incorporation of these sludges in rustic stoneware products.

The results of thermal analysis (DTA and TG) of the raw materials tested in this work are shown in Fig. 2(a) and (b), respectively. The DTA/TG behaviour of RC is typical of kaolinitic/illitic clays, which is consistent with the presence of kaolinite and muscovite.¹⁴ At about 120 °C, an endothermic

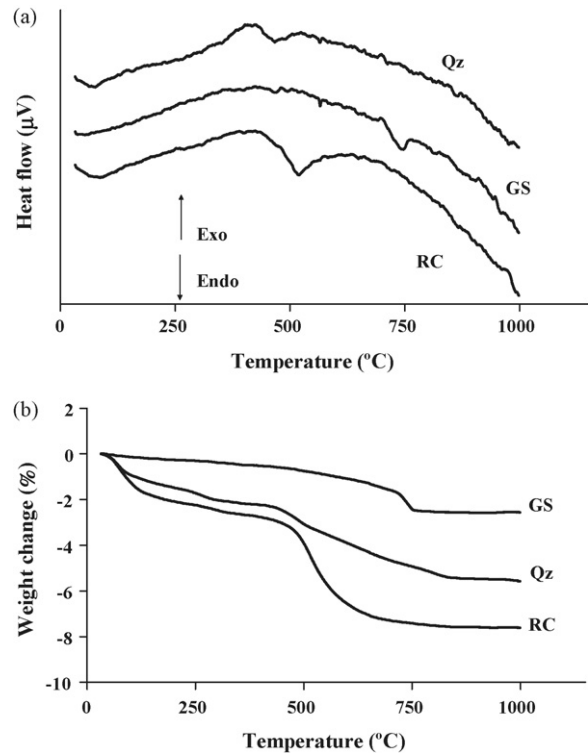


Fig. 2. Thermal analysis curves, DTA (a) and TG (b), of RC, Qz and GS.

Table 3
Chemical composition of the raw materials (wt.%)

Oxide	Red clay (RC)	Granite sludge (GS)	Quartzite (Qz)
SiO ₂	60.27	67.09	68.48
Al ₂ O ₃	20.11	13.73	14.93
Fe ₂ O ₃	7.53	2.26	4.68
CaO	0.15	4.16	0.11
MgO	0.76	0.81	0.78
Na ₂ O	0.19	3.50	0.31
K ₂ O	2.10	4.62	2.94
TiO ₂	1.14	0.24	1.08
MnO	0.07	0.04	0.07
P ₂ O ₅	0.18	0.28	0.21
LoI	6.40	3.00	5.50

peak occurs due to the release of adsorbed water, accompanied by 2% weight loss. Between 200 °C and 470 °C, there is a weight loss of 1%, due to the decomposition of organic matter, which is translated in the DTA curve by a broad exothermic band. This is then followed by an endothermic peak centred at 520 °C, attributed to the desidroxilation of kaolinite, with 4% weight loss. At 980 °C, an exothermic peak of low intensity corresponding to the mullite nucleation is observed. The total weight loss of RC clay is about 7%.

The DTA/TG curves of Qz are very similar to those of RC, differing mostly in peaks intensity (lower). The peaks also appear centred at temperatures that are slightly different. The total weight loss for this sludge is about 6%. The DTA curves of Qz and GS show low intensity endothermic peaks at 570 °C, which are associated to the quartz transformation.¹⁵ Besides this peak, GS also shows a main endothermic peak centred at 740 °C, which is consistent with the presence of illite–muscovite-like minerals and calcium carbonate detected by XRD, the decomposition of which originates a weight loss of 1%.¹⁴ A low intensity endothermic band observed in the temperatures range of about 860–900 °C can also be attributed to the calcite decomposition, while a slight exothermic peak appearing at 975 °C is due to the nucleation of mullite. The total weight loss of GS sludge is 3%.

The data of chemical composition and loss on ignition of the raw materials are presented in Table 3. It can be observed that SiO₂ is the predominant oxide, followed by Al₂O₃. GS has a high total content (10.38%) of fluxing oxides (K₂O + Na₂O + Fe₂O₃), being more prone to form larger amounts of a glassy phase upon sintering. Qz presents a lower total amount (7.93%) of fluxing oxides, being therefore expected to confer to the pastes a higher refractoriness in comparison to QS. All the raw materials used contain appreciable amounts of F₂O₃, and besides its fluxing role, it also confers to the fired products the characteristic reddish colour.

3.2. Technological characterization of the formulated products

As referred above, the formation a liquid phase during sintering is essential to promote densification. Depending on the liquid viscosity, it tends to fulfil the cavities of the ceramic body, reducing its porosity.¹⁶ The viscosity is a function of the ratio between

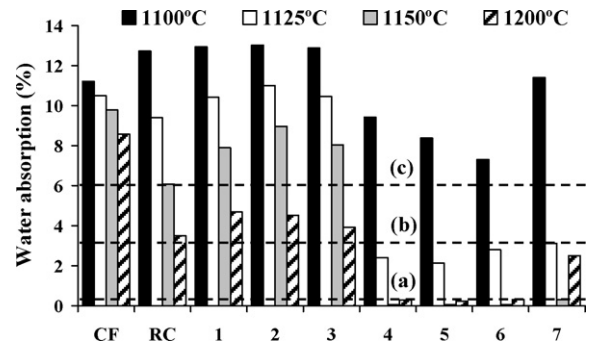


Fig. 3. Comparison of water adsorption values and its dependence on sintering temperature for all the samples presented in Table 1, after firing for 1 h. The horizontal dashed lines are the limits stipulated for the ISO 13006 standard groups: (a) BIIa, (b) BIIb and (c) BIIc.

the glass former oxides (SiO₂ or Al₂O₃) and the modifier oxides like K₂O and Na₂O (excellent fluxing agents). It is also a function of the ratio between these last ones. The main difference between these two fluxing agents is that, while K₂O forms eutectics at low temperatures, Na₂O has a more pronounced effect on decreasing the viscosity.¹⁷

Figs. 3–5 present the results of technological properties of the samples from different formulations as a function of the sintering temperatures. Fig. 3 shows that water absorption decreases for every composition with the increase of sintering temperature, except for formulations comprising GS (4, 5, 6, and 7) sintered at 1200 °C, the values of which increase suggesting over-firing phenomena. It is clear that the samples made of

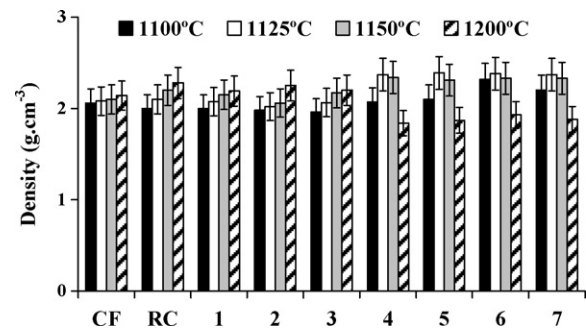


Fig. 4. Density of the samples after firing at different temperatures for 1 h.

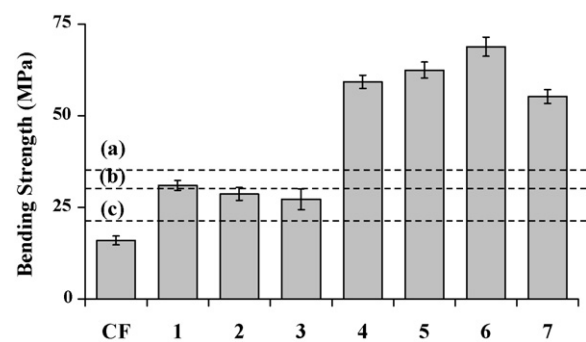


Fig. 5. Bending strength of samples sintered at 1150 °C for 1 h. The horizontal dashed lines are the limits stipulated for the ISO 13006 standard groups: (a) BIIa, (b) BIIb and (c) BIIc.

reference paste are the ones that exhibit the higher water absorption values after firing at the two higher temperatures (1150 °C and 1200 °C). When sintering is carried out at the two lower temperatures (1100 °C and 1125 °C) at which the quartzite sludge still behaves mostly like an inert filler, the samples of formulations 1, 2 and 3 exhibit a higher water absorption capacity in comparison to the reference paste. Fig. 3 also reveals that, except at the lowest sintering temperature, the samples made of red clay RC present water absorption values that are systematically lower in comparison to those of reference paste, suggesting a better sintering behaviour. The water absorption capacity is a property directly related with the type of microstructure developed during sintering. It can be therefore regarded as a simple way to predict the technological properties of the final products. At 1150 °C, the compositions 4, 5, 6 and 7 present water absorption values corresponding to those of stoneware pressed pavements classified by the international standard ISO 13006 as belonging to the group BIa. The accentuated decrease of water absorption observed with the introduction of GS reflects the effects of its higher total amount of fluxing agents (Fe_2O_3 , K_2O and Na_2O) contributing to a more extensive formation of liquid phase and to a significant reduction of porosity. The samples of formulations 1, 2 and 3 sintered at 1200 °C present water absorption values that permit to classify them according to the ISO 13006 group BIIa.¹⁸

The evolution of the apparent density of each formulation with sintering temperature is presented in Fig. 4. Apparent density permits to evaluate the sintering status of the material and anticipates the microstructure of the final product. The apparent density of the reference paste, clay RC, and of the formulations 1, 2 and 3 tend to systematically increase with sintering temperature increasing, in good agreement with the observed water absorption values Fig. 3. On the other hand, formulations 4, 5, 6, and 7 comprising GS reached maximum density values at 1125 °C, followed by a slight decrease at 1150 °C and a more clear decreasing trend as the sintering temperature further increased to 1200 °C. Crossing this information with Fig. 3, the simultaneous decrease of apparent density and water absorption values observed for formulations comprising GS when sintering temperature increases from 1125 °C to 1150 °C, can suggest contradictory results. However, these results can be explained by the formation of closed porosity that turns samples impermeable to water, contributing for the decrease of water absorption values. Moreover, some phases with lower density such as mullite and glassy phase can occur at 1150 °C, contributing to the decrease of apparent density values. At 1200 °C, the significant decrease of density is mainly the result of over-firing phenomena.

Fig. 5 compares the results of three-point bending strength of all the samples sintered at 1150 °C. It is interesting to note that the reference paste CF is the one that presents the lowest values of mechanical properties. The measured data of water absorption and flexural strength are in close agreement to the results indicated by the supplier, but do not fit even the less demanding standard BIIa ISO 13006 for stoneware products (see Figs. 3 and 5). A slight apparent decreasing trend is observed among the formulations 1–3 containing Qz sludge. This

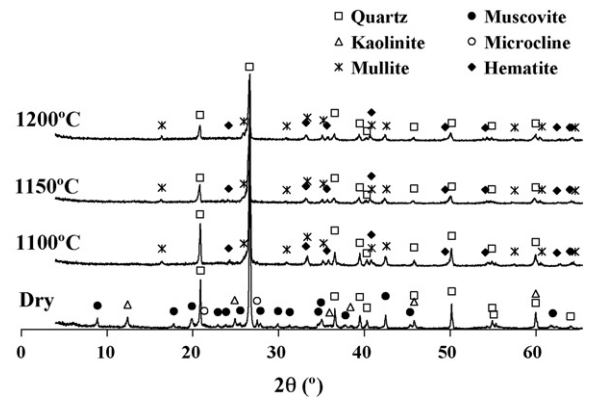


Fig. 6. XRD spectra of formulation 2 before and after firing at different temperatures for 1 h.

decreasing trend was not expected since the RC weight ratio increases from 30 to 40% from the formulation 1 to 3, although it shows some consistence with the measured values of water absorption. The formulations containing GS (4, 5, 6, and 7) are significantly stronger in comparison to the other compositions. The measured values are well above the minimum values stipulated for group BIa of the ISO standard 13006, which is directed to the porcelain tiles made by dry-powder pressing, whereby water absorption must be less than 0.5% and three point bend-

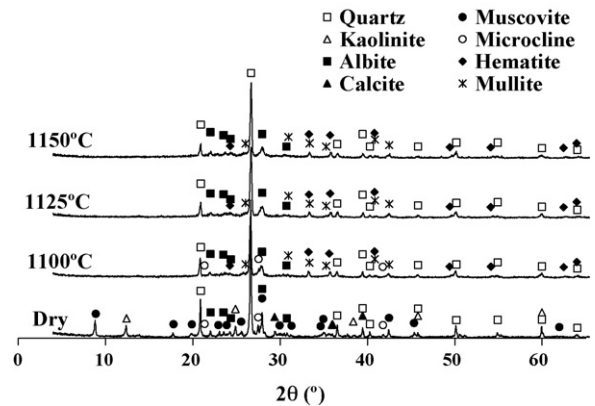


Fig. 7. XRD spectra of formulation 5 before and after firing at different temperatures for 1 h.

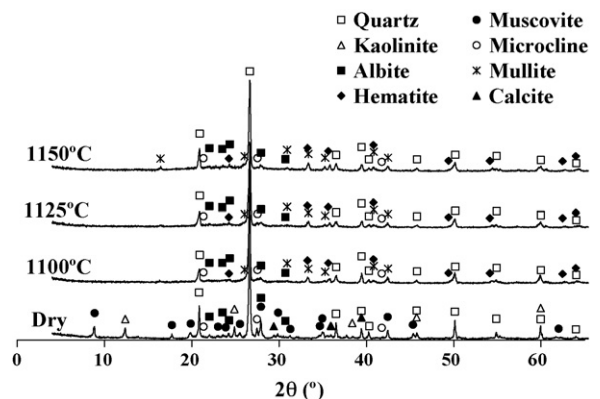


Fig. 8. XRD spectra of formulation 7 before and after firing at different temperatures for 1 h.

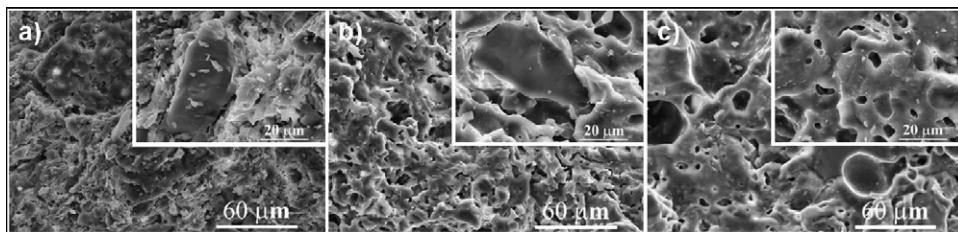


Fig. 9. SEM photomicrographs of fracture surfaces of samples of formulation 2 sintered at different temperatures: (a) 1100 °C; (b) 1150 °C; (c) 1200 °C.

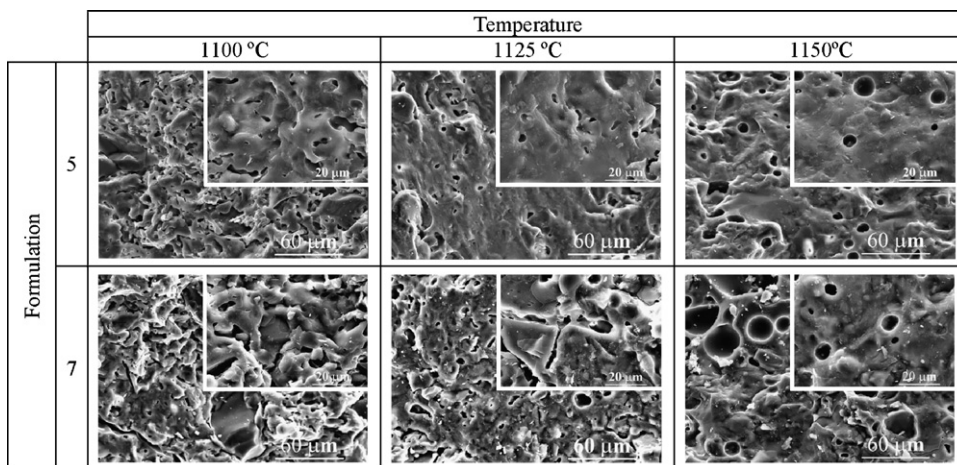


Fig. 10. SEM photomicrographs of fracture surfaces of samples of formulations 5 and 7 sintered at the three different indicated temperatures of 1100 °C, 1125 °C, and 1150 °C.

ing strength higher than 35 MPa.¹⁸ Moreover, a clear increasing trend is observed with the RC weight ratio increasing from 30% to 40% (formulations 4, 5, and 6), as expected. The replacement of half of the GS in the formulation 4 by an equivalent amount of Qz sludge (formulation 7) resulted in a decrease of flexural strength of about 7% and an increase of water absorption. Therefore, it is possible to conclude that the results of mechanical properties are in accordance with the values obtained for water absorption and density, showing that formulations comprising granite sludge present higher mechanical resistance and the corresponding lower water absorption and higher density values.

Figs. 6–8 present the X-ray spectra of the compositions 2, 5 and 7 before and after sintering at 1000 °C, 1150 °C and 1200 °C. It can be observed that kaolinite and muscovite existing in the green bodies disappeared after firing at 1100 °C, while mullite and hematite appeared as new crystalline phases. The intensity of the peaks corresponding to the fluxing minerals (microcline and albite) tends to diminish as the temperature increases, while quartz is gradually dissolved in the vitreous phase. As expected, the intensity of the quartz peaks is stronger in the formulations 2 and 7, more refractory and richer in Qz sludge. Fig. 9 shows SEM images of fracture surfaces of samples of formulation 2 sintering at 1000 °C, 1150 °C and 1200 °C, while Fig. 10 shows SEM images of fracture surfaces of samples of formulations 5 and 7 sintering at 1000 °C, 1125 °C and 1150 °C. For all compositions tested, a porosity reduction as sintering temperature increases is clearly observed, which is associated with the increased amount of the vitreous phase and the concomitant densification process.

The densification process occurs at higher temperatures in the case of composition 2, and at lower temperatures in the case of composition 5, with composition 7 showing an intermediate behaviour, as expected. The morphology of the pores is still irregular at 1100 °C and then evolves to a spherical shape as sintering temperature increases. Spherical pores are usually formed in matrices rich in a vitreous phase. These results suggest that the amount of liquid phase formed within the temperature range of 1125–1150 °C shall be enough to promote a good level of densification, especially in the case of compositions containing granite sludge. This hypothesis is supported by the water absorption results (Fig. 3) and apparent density (Fig. 4).

4. Conclusions

The results presented and discussed along this report enable the following conclusions to be drawn:

1. As has been postulated, the inexpensive granite and quartzite sludges proved to be good substitutes for costly raw materials, therefore preserving the mineral resources, solving environmental problems, while lowering the production costs.
2. Being constituted mainly by very thin particles ($\phi < 100 \mu\text{m}$), these residues can be directly incorporated in industrial compositions, avoiding energy costs related with milling processes, as well as with the maintenance and erosion of the milling equipment.
3. This work proves that much better final properties of the ceramic body could be achieved with simple formulations

involving just 30–40 wt.% of a plastic clay of suitable chemical and mineralogical compositions and 70–60 wt.% of one of the tested sludges or their mixtures, and that depositing this kind of residues in landfill is a big environmental and economic mistake.

4. Granite sludge has a high content of total fluxing oxides that favour the maturation of the ceramic body at lower sintering temperatures, being a good substitute for feldspar in stoneware tile products that satisfy the most demanding requirements of the group BIa of the ISO 13006 standard.
5. The incorporation of quartzite residues allows to obtain semi-porous ceramic bodies with water absorption values between 3.5% and 4.7%, within the range BII (3–6%) of the standard ISO 13006.
6. A combination of granite and quartzite residues enables to obtain ceramic stoneware bodies satisfying the requirements of the group BIb of the ISO 13006 standard.

Acknowledgement

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